III.A.8 Continuous Process for Low-Cost, High-Quality YSZ Powder

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Objectives

- Develop a robust process for producing yttrium-stabilized zirconia (YSZ) powder that can be tailored to meet the Solid State Energy Conversion Alliance (SECA) industry team needs.
- Produce YSZ powder in 5-10 kg batches, and demonstrate reproducibility of the process.
- Demonstrate the advantages of tailoring YSZ powder characteristics to specific requirements of fabrication processes used in solid oxide fuel cell (SOFC) manufacture.
- Demonstrate that the process provides YSZ powder at low manufacturing cost.

Approach

- Use chemical precipitation methods to produce hydroxide precursors that can be converted into crystalline YSZ via thermal treatments.
- Use ball milling and attrition milling methods to reduce particle size of YSZ powders to below one micron.
- Use uniaxial and isostatic pressing methods followed by sintering to fabricate ceramic samples for density and ionic conductivity measurements.

Accomplishments

- Established a homogeneous precipitation process for preparing an yttrium-zirconium hydrous oxide precursor, which can be converted to crystalline YSZ via calcination.
- Established calcination and milling methods to prepare YSZ powders with controlled surface area and particle size distribution.
- Demonstrated that YSZ powder produced by the process can be sintered to densities greater than 98 percent theoretical at temperatures less than 1400ºC.
- Demonstrated sintered YSZ ceramics with high ionic conductivity (>0.04 S/cm at 800ºC), equivalent to the best values reported in the literature.
- Demonstrated a high surface area and fine particle size grade of YSZ powder that can be sintered at ultra-low temperatures (1200 to 1250°C).
- Demonstrated that the manufactured cost of YSZ powder produced using the process will be less than $25 per kilogram at large production volumes.

Future Directions

- Continued process refinements aimed at increasing performance and reducing manufacturing costs.
- Demonstration of advantages of using tailored YSZ powders in fabrication processes used for the manufacture of SOFCs. Planar and tubular SOFC components will be fabricated using tailored YSZ powder, and these components will be characterized and tested.

- Production of evaluation samples of YSZ electrolyte powder, NiO/YSZ anode powder, and/or SOFC components produced from these powders, for evaluation by SECA's industry teams.
- Continual updates to the manufacturing cost analyses, incorporating process refinements that are implemented.

Introduction

One of the current barriers to reducing the manufacturing cost of SOFCs is the high cost of some of the critical raw materials. The availability of a low-cost, highly reliable and reproducible supply of engineered raw materials is needed to assure successful commercialization of SOFC technology. The yttrium-stabilized zirconia (YSZ) electrolyte material is a primary ingredient for two of the three layers comprising an SOFC element: the dense electrolyte layer and the porous nickel-based cermet (Ni/YSZ) anode layer. In addition, YSZ often is used as a performance-enhancing additive to lanthanum strontium manganite (LSM) based cathode layers. In practice, the same YSZ raw material is used for each of the component layers, even though different fabrication processes are used for each layer. Significant opportunities for performance optimization and cost reduction would be possible if the YSZ raw material were tailored for each component layer. The project focuses on the development of synthesis technology for YSZ powder that is "tailored" to the process-specific needs of different SOFC designs being developed under DOE's SECA program.

Approach

NexTech's approach to developing a low-cost YSZ electrolyte powder production process is based on the following principles: (1) the process must be scaleable to high volume (500 tons per year) at a cost of less than \$25/kilogram; (2) the process must be sufficiently versatile so that powder characteristics can be tailored to a specific customer's requirements; (3) the process must be reliable, providing consistent batch-to-batch quality; and (4) the process must provide a relatively pure YSZ powder that meets performance criteria relative to particle size, surface area, sintering activity, and ionic conductivity. The process being developed in this project is based on homogeneous precipitation (see Figure 1). With homogeneous precipitation, the pH and solids content remain constant throughout the process, which is the key to achieving uniformity and reproducibility of the finished product. Another attribute of the homogeneous precipitation process is that it can be made continuous with constant replenishment of the feed solutions. This provides considerable cost and reliability advantages relative to current chemical synthesis processes.

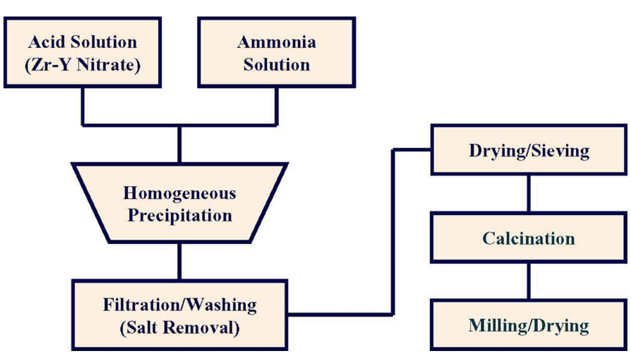

Figure 1. Homogenous Precipitation Process for YSZ Powder

In the project, synthesis studies are being conducted to identify optimum precipitation conditions for producing hydrous oxide precursors. These precursors then are processed into YSZ powders by washing and drying of the precipitates, calcination of the dried precursor to form a crystalline YSZ powder with targeted surface area (~10 m^2/gram), and milling of the calcined YSZ powder to sub-micron particle size. The YSZ powders are subjected to a comprehensive characterization protocol, involving x-ray diffraction, chemical analyses, particle size distribution, surface area measurements, and sintering studies. Performance of sintered YSZ ceramics is being assessed by density measurements, ionic conductivity measurements, mechanical property measurements, and scanning electron microscopy.

Results to Date

In this project, NexTech has demonstrated a laboratory-scale continuous (homogeneous) precipitation process for YSZ electrolyte powder

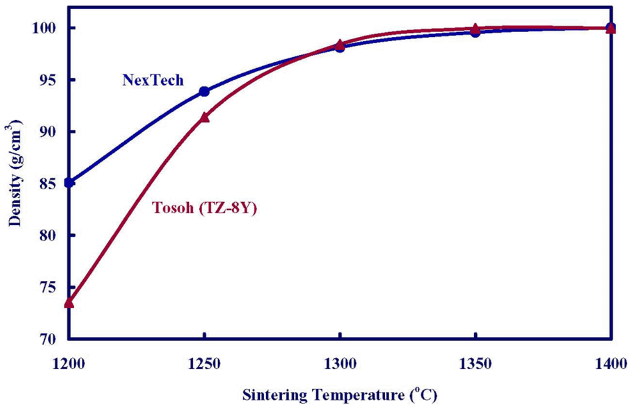

Figure 2. Sintering Performance of NexTech's YSZ Powder (baseline process), Compared to Commercially Available YSZ Powder (Tosoh, TZ-8Y)

with equivalent, and in some ways superior, performance to YSZ powder that is commercially available from non-domestic suppliers. Key results to date are discussed below:

- The initial precipitation conditions were shown to have a profound effect on the performance of fully processed (calcined and milled) YSZ powders. After optimization of precipitation conditions, YSZ powders produced by NexTech's baseline process sinter to high densities (>98 percent theoretical) at temperatures of 1300ºC and higher. The NexTech powder also exhibits improved low-temperature sinterability compared to commercial powder (Tosoh, TZ-8Y) with similar surface area (see Figure 2).
- NexTech demonstrated reproducibility of its synthesis process by producing three separate batches of YSZ powder and characterizing these powders through all stages of processing. Particle size distribution measurements (see Figure 3) indicated average particle sizes of 0.30, 0.27 and 0.31 microns, and surface areas of the three powders ranged from 13.9 to 14.5 m^2/gram. Sintering performance and ionic conductivity were identical for the three batches (within experimental error of the measurements).
- NexTech demonstrated improved densification through doping with alumina (Al_2O_3), nickel oxide (NiO), manganese oxide (Mn_2O_3) and cobalt oxide (CoO) dopants, especially at low sintering temperatures (less than 1300ºC).

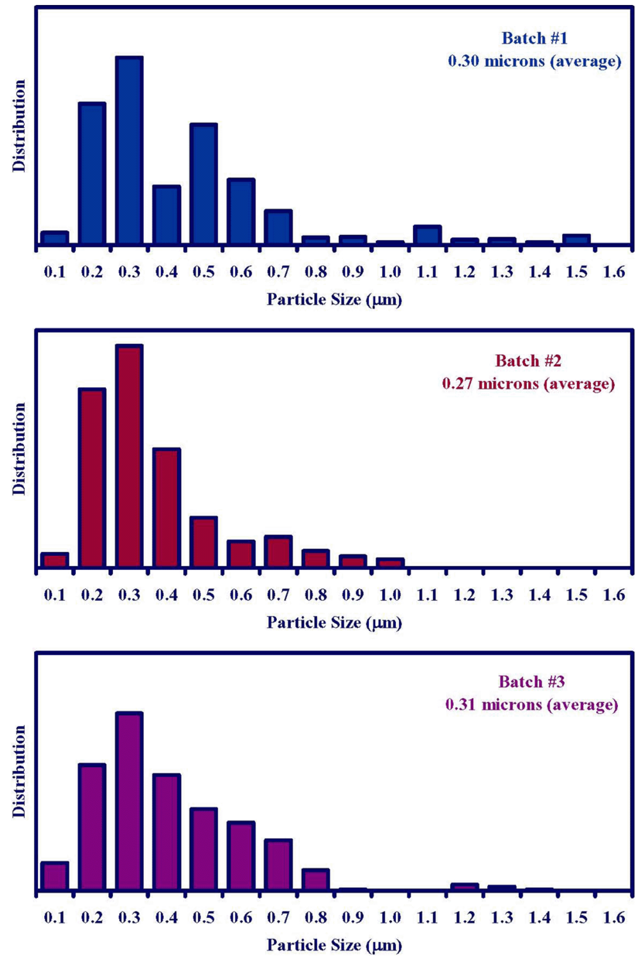

Figure 3. Particle Size Distributions of YSZ Powder from Three Separate Batches

NiO and Mn_2O_3 dopants resulted in significant depression of ionic conductivity, whereas this effect was less pronounced with Al_2O_3 and CoO dopants (depending on the dopant amount and method of incorporation). Results obtained with CoO dopants are presented in Figures 4 and 5. With a 0.1 wt% addition of CoO, the sintering temperature was reduced by about 50°C, with little change in ionic conductivity at 800°C. With increased cobalt doping (1 wt%), the sintering performance is further improved, but with a significant loss of ionic conductivity.

- NexTech's synthesis process also was demonstrated for scandium-stabilized zirconia (ScSZ) electrolyte compositions, both partially stabilized ScSZ-6 and fully stabilized ScSZ-10 compositions. The increased conductivity of ScSZ electrolytes was confirmed (see Figure 6).

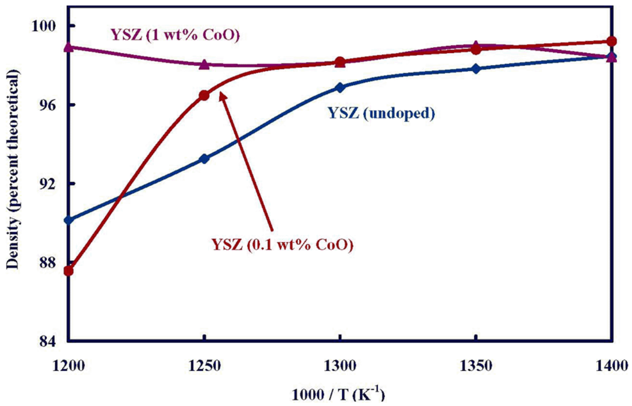

Figure 4. Effect of Cobalt Doping on Sintering Performance of YSZ Powder

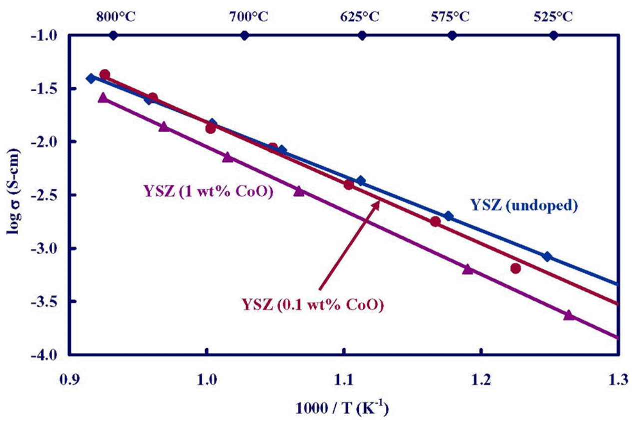

Figure 5. Effect of Cobalt Doping on Ionic Conductivity of Sintered YSZ Ceramics

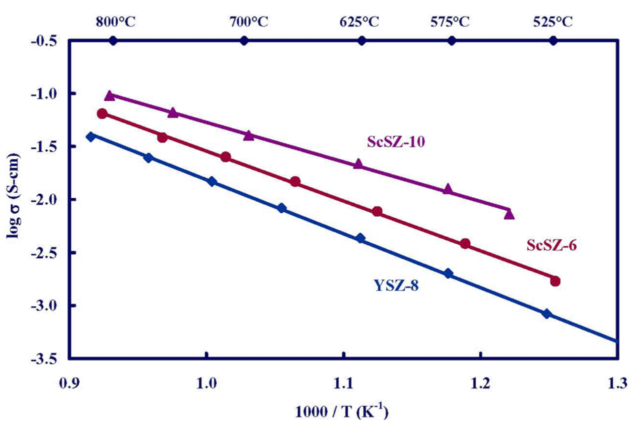

Figure 6. Ionic Conductivity of Yttrium-Stabilized and Scandium-Stabilized Zirconia Ceramics

- A manufacturing cost analysis confirmed that YSZ powder prepared by NexTech's homogeneous precipitation process could be manufactured at a cost of less than $25 per kilogram (see Figure 7). This analysis was based on a production volume of 500 metric tons per year, which is a fraction of the volume necessary when SOFCs are in full-scale production.

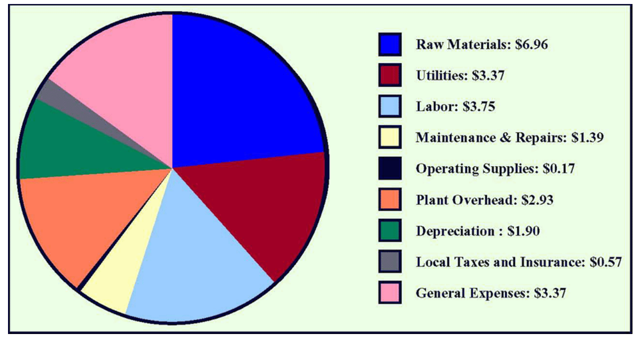

Figure 7. Results of Manufacturing Cost Analysis

Conclusions

- Homogeneous precipitation is a promising route for the continuous synthesis of hydrous oxide precursors to high-quality YSZ powders. The initial precipitation conditions have a profound effect on downstream milling performance (after calcination) and on subsequent sintering and electrical performance. Important synthesis variables include concentrations of the precipitant solutions, feed rates during precipitation, and the pH during precipitation.
- The processing of the precipitated hydroxide slurries prior to drying was critically important to achieving high-performance YSZ powders. For aqueous processing, surfactants were required to allow hydroxide precipitates to be dried directly from aqueous suspensions. An alternative approach, based on solvent exchange of the precipitated hydroxides into isopropyl alcohol prior to drying, also was demonstrated.
- Several oxide dopant strategies were identified that led to significant improvements in sintering performance of YSZ ceramics. Dopants such as aluminum oxide, nickel oxide, cobalt oxide, and manganese oxide all were found to increase ceramic densities, especially with low sintering temperatures (~1200 to 1300ºC). Aluminum and cobalt oxide dopants were the most effective for reducing sintering temperature without adversely affecting ionic conductivity.

- Based on a manufacturing cost analysis, YSZ powders prepared by the homogeneous precipitation process can be manufactured at a cost of less than $25 per kilogram at high production volumes. This analysis identified specific unit operations where cost can be reduced upon further optimization.

FY 2005 Publications/Presentations

1. S.L. Swartz, et al., *Continuous Process for Low-Cost, High-Quality YSZ Powder*, SECA Core Technology Workshop (Tampa, Florida, January 27, 2005).